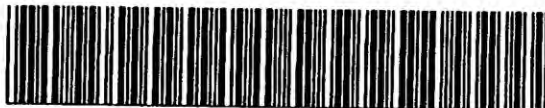


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(54) Title: BLENDS OF POLYCARBONATE AND ETHYLENE POLYMERS			
(57) Abstract  A blend of polycarbonate and a substantially linear ethylene polymer which has a desirable balance of impact and solvent resistance properties.			

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### Blends of Polycarbonate and Ethylene Polymers

This invention relates to compositions containing polycarbonate and a substantially linear ethylene polymer.

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Polycarbonate has found many uses because, in general, it combines a high level of heat resistance and dimensional stability with good insulating and non-corrosive properties, and it is easily molded. It does, however, suffer from a tendency to craze and crack under the effects of contact with organic solvents such as gasoline. An undesirable result in polycarbonate which has crazed is that it is more likely to experience brittle rather than ductile failure. This disadvantage has been somewhat relieved by the practice of blending polycarbonate with various olefin polymers such as low density polyethylene or linear low density polyethylene, or thermoplastic rubbers such as ethylene/propylene copolymer. These added substances are capable of improving the resistance of polycarbonate to solvents, but they tend to delaminate and cause an offsetting reduction in the toughness, impact resistance and weldline strength of the blended polycarbonate composition. Such delamination, and the resulting loss of utility, is reported, for example, in US 4,496,693.

Impact resistance in polycarbonate can be improved by the incorporation of emulsion or core-shell elastomers such as methacrylate/butadiene/styrene copolymer or a butyl acrylate rubber. However, these core-shell rubbers hinder processability of the blend by increasing viscosity and impart no improvement to the solvent resistance of polycarbonate. It would accordingly be desirable if modifiers blended with polycarbonate for the purpose of improving its solvent resistance did not also deleteriously affect its toughness and impact and weldline strength, and cause delamination as evidenced by peeling or splintering in a molded article.

In one aspect, this invention consequently involves a composition of matter containing, in admixture, polycarbonate and a substantially linear ethylene polymer. In another aspect, this invention involves the inclusion with such a composition of a styrenic

copolymer, a supplemental impact modifier and/or an additional molding polymer.

It has been found that articles molded from the compositions of this invention show no tendency toward delamination and exhibit a desirable balance of surprisingly high levels of impact resistance, solvent resistance and processability.

The compositions of this invention are useful, for example, in the production of films, fibers, extruded sheets, multi-layer laminates and molded or shaped articles of virtually all varieties, especially data storage apparatus, appliance and instrument housings, motor vehicle body panels and other parts and components for use in the automotive, electrical and electronics industries.

The compositions of this invention are those in which (a) polycarbonate has been admixed in a polymeric blend with (b) a substantially linear ethylene polymer. The compositions of this invention may, optionally, also contain (c) a styrenic copolymer, (d) a supplemental impact modifier, and (e) one or more additional molding polymers. Suitable ranges of content for components (a) and (b) in the compositions of this invention, and suitable ranges of content for components (c), (d) and (e) if and when they are present, expressed in parts by weight of the total composition, are as follows:

- (a) polycarbonate at least about 60 parts, advantageously at least about 70 parts, and preferably at least about 80 parts, and yet not more than about 99 parts, advantageously not more than about 98 parts, and preferably not more than about 95 parts;
- (b) substantially linear ethylene polymer at least about 1 parts, advantageously at least about 2 parts, and preferably at least about 5 parts, and yet not more than about 40 parts, advantageously not more than about 30 parts, and preferably not more than about 20 parts;
- (c) styrenic copolymer at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts, and yet not more than about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably not more than about 45 parts;

- (d) supplemental impact modifier at least about 0.1 parts, advantageously at least about 0.5 parts, preferably at least about 1 parts, and more preferably at least about 3 parts, and yet not more than about 25 parts, advantageously not more than about 20 parts, preferably not more than about 15 parts, and more preferably not more than about 10 parts; and
- (e) molding polymer at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts, and yet not more than about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably not more than about 45 parts.

The number of weight parts of the various components from which the compositions of this invention may be prepared may, but need not necessarily, total to 100 weight parts.

Also included within this invention are the reaction products, if any, of the above named components when admixed in the compositions of this invention.

Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. When softened or melted by the application of heat, the compositions of this invention are useful for fabrication and can be formed or molded using conventional techniques.

Component (a) in the compositions of this invention is a polycarbonate, which can be prepared from a dihydroxy compound such as a bisphenol, and a carbonate precursor such as a disubstituted carbonic acid derivative, a haloformate (such as a bishaloformate of a glycol or dihydroxy benzene), or a carbonate ester such as diphenyl carbonate or a substituted derivative thereof. These components are often reacted by means of the phase boundary process in which the dihydroxy compound is dissolved and deprotonated in an aqueous alkaline solution to form bisphenolate and the carbonate precursor is dissolved in an organic solvent. The aqueous alkaline solution often has a pH in excess in excess 8.0 or 9.0, and can be formed in water from a caustic soda, such as NaOH, or from other bases such as those included in the alkali metal and alkaline earth metal phosphates, bicarbonates, oxides and

hydroxides. Base is typically used in an amount of about 2 to 4, preferably about 3 to 4, moles per mole of dihydroxy compound.

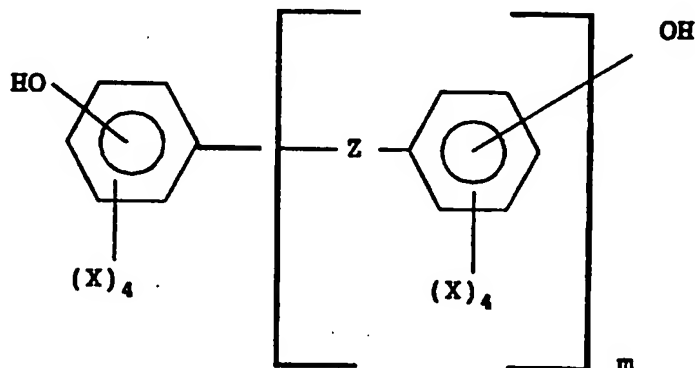
These components are often reacted by means of a mixture prepared initially from the aromatic dihydroxy compound, water and a non-reactive organic solvent immiscible with water selected from among those in which the carbonate precursor and polycarbonate product are soluble. Representative solvents include chlorinated hydrocarbons such as methylene chloride, 1,2-dichloroethane, tetrachloroethane, chlorobenzene, and chloroform. Caustic soda or other base is then added to the reaction mixture to adjust the pH of the mixture to a level at which the dihydroxy compound is activated to dianionic form.

A carbonate precursor is contacted with an agitated mixture of the aqueous alkaline solution of the dihydroxy compound, and, for such purpose, the carbonate precursor can be bubbled into the reaction mixture in the form of a gas, or can be dissolved and introduced in solution form. Carbonate precursor is typically used in an amount of about 1.0 to 1.8, preferably about 1.2 to 1.5, moles per mole of dihydroxy compound. The mixture is agitated in a manner which is sufficient to disperse or suspend droplets of the solvent containing the carbonate precursor in the aqueous alkaline solution. Reaction between the organic and aqueous phases created by such agitation yields the bis(carbonate precursor) ester of the dihydroxy compound. For example, if the carbonate precursor is a carbonyl halide such as phosgene, the products of this initial phase of the process are monomers or oligomers which are either mono- or dichloroformates, or contain a phenolate ion at each terminus.

These intermediate mono- and oligocarbonates dissolve in the organic solvent as they form, and they can then be condensed to a higher molecular weight polycarbonate by contact with a coupling catalyst such as a tertiary amine. Such a catalyst may be added to the reaction mixture before or after a dihydroxy compound is contacted with a carbonate precursor, and is typically used in an amount of about 0.01 to 0.1 moles per mole of dihydroxy compound.

The polycarbonate forming reaction can be run at a pH from above 7.0 to about 14, and at a temperature between 0°C to 100°C, although usually not in excess of the boiling point (reflux temperature) of the solvent used. Frequently, the reaction is run at a temperature of about 0°C to about 45°C. Upon completion of polymerization, the organic and aqueous phases are separated to allow washing and purification of the organic phase and recovery of the polycarbonate product by devolatilization or precipitation.

Examples of some dihydroxy compounds suitable for the preparation of polycarbonate include variously bridged, substituted or unsubstituted aromatic dihydroxy compounds (or mixtures thereof) represented by the formula



wherein:

- (I) Z is (A) a divalent radical, of which all or different portions can be (i) linear, branched, cyclic or bicyclic, (ii) aliphatic or aromatic, and/or (iii) saturated or unsaturated, said divalent radical being composed of 1-35 carbon atoms together with up to five oxygen, nitrogen, sulfur, phosphorous and/or halogen (such as fluorine, chlorine and/or bromine) atoms; or (B) S, S<sub>2</sub>, SO, SO<sub>2</sub>, O or CO; or (C) a single bond;
- (II) each X is independently hydrogen, a halogen (such as fluorine, chlorine and/or bromine), a C<sub>1</sub>-C<sub>12</sub>, preferably C<sub>1</sub>-C<sub>8</sub>, linear or cyclic alkyl, aryl, alkaryl, aralkyl, alkoxy or aryloxy

radical, such as methyl, ethyl, isopropyl, cyclopentyl, cyclohexyl, methoxy, ethoxy, benzyl, tolyl, xylyl, phenoxy and/or xylynoxy; or a nitro or nitrile radical; and

(III)  $m$  is 0 or 1.

5

For example, the bridging radical represented by  $Z$  in the above formula can be a  $C_2$ - $C_{30}$  alkyl, cycloalkyl, alkylidene or cycloalkylidene radical, or two or more thereof connected by an aromatic or ether linkage, or can be a carbon atom to which is bonded one or more groups such as  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $n$ - $C_3H_7$ ,  $i$ - $C_3H_7$ , cyclohexyl, bicyclo[2.2.1]heptyl, benzyl,  $CF_2$ ,  $CF_3$ ,  $CCl_3$ ,  $CF_2Cl$ ,  $CN$ ,  $(CH_2)_2COOCH_3$ , or  $PO(OCH_3)_2$ .

Representative examples of dihydroxy compounds of particular interest are the bis(hydroxyphenyl)alkanes, the bis(hydroxyphenyl)cycloalkanes, the dihydroxydiphenyls and the bis(hydroxyphenyl)sulfones, and in particular are 2,2-bis(4-hydroxyphenyl)propane ("Bisphenol-A" or "Bis-A"); 2,2-bis(3,5-dihalo-4-hydroxyphenyl)propane ("Tetrahalo Bisphenol-A") where the halogen can be fluorine, chlorine, bromine or iodine, for example 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane ("Tetrabromo Bisphenol-A" or "TBBA"); 2,2-bis(3,5-dialkyl-4-hydroxyphenyl)propane ("Tetraalkyl Bisphenol-A") where the alkyl can be methyl or ethyl, for example 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane ("Tetramethyl Bisphenol-A"); 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-AP" or "Bis-AP"); Bishydroxy phenyl fluorene; and 1,1-bis(4-hydroxyphenyl)cyclohexane.

Using a process such as is generally described above, a polycarbonate product can be obtained having a weight average molecular weight, as determined by light scattering or gel permeation chromatography, of 8,000 to 200,000 and preferably 15,000 to 40,000, and/or a melt flow value of about 3 to 150, preferably about 10 to 80 (as determined by ASTM Designation D 1238-89, Condition 300/1.2), although values outside these ranges are permitted as well. Molecular weight can be controlled by addition to the reaction mixture of a chain terminator which may be selected from monofunctional substances such as phenols, alcohols, amines, imides, carbonic acid chlorides, sulfonic acid chlorides, benzyltriethyl ammonium chloride, or



phenylchlorocarbonates. A chain terminator may be added to the reaction mixture before or after a dihydroxy compound is contacted with a carbonate precursor, and is typically used in an amount of about 0.01 to 0.1 moles per mole of dihydroxy compound.

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A branched rather than linear polycarbonate molecule can be obtained by adding to the reaction mixture a tri- or polyfunctional monomer such as trimellitic acid or trisphenoxy ethane.

10

Also included within the term "polycarbonate", as used herein, are various copolycarbonates, which can be prepared by incorporating two or more different dihydroxy compounds into the reaction mixture; or a poly(ester/carbonate), which can be prepared by incorporating an ester-forming compound such as terephthalic acid into the reaction mixture. In a preferred embodiment, however, the compositions of this invention exclude a poly(ester/carbonate).

15

The methods generally described above for preparing carbonate polymers suitable for use in the practice of this invention are well known; for example, several methods are discussed in detail in Schnell, USP 3,028,365; Glass, USP 4,529,791; and Grigo, USP 4,677,162, each of which is incorporated as a part hereof.

20

Component (b) in the compositions of this invention is a substantially linear ethylene polymer, or a mixture of more than one thereof. These substantially linear ethylene polymers are known, and they and their method of preparation are fully described in USP 5,272,236 and USP 5,278,272, both of which are incorporated herein by reference. As here used, "substantially linear" means that the polymer backbone is substituted with about 0.01 long-chain branches/1000 carbons to about 3 long-chain branches/1000 carbons, preferably from about 0.01 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons, more preferably from about 0.05 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons. Long-chain branching is here defined as a chain length of at least about 6 carbon atoms, above which the length cannot be distinguished using  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy, yet the long-chain branch can be about the same length as the length of the polymer backbone.

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These substantially linear ethylene polymers are prepared by using constrained geometry catalysts, and are characterized by a narrow molecular weight distribution and, if an interpolymer, by a narrow comonomer distribution. As here used, "interpolymer" means a polymer of two or more comonomers, for example a copolymer or terpolymer, such as might be prepared by polymerizing ethylene with at least one other comonomer. Other basic characteristics of these substantially linear ethylene polymers include a low residuals content (i.e. a low concentration therein of the catalyst used to prepare the polymer, unreacted comonomers and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability even though the molecular weight distribution is narrow relative to conventional olefin polymers.

15

While the substantially linear ethylene polymers used in the practice of this invention include substantially linear ethylene homopolymers, preferably the substantially linear ethylene polymers comprise between about 50 to 95 weight percent ethylene and about 5 to 50, and preferably 10 to 25, weight percent of at least one alpha-olefin comonomer. The comonomer content is measured using infrared spectroscopy according to ASTM D-2238, Method B. Typically, the substantially linear ethylene polymers are copolymers of ethylene and one or more alpha-olefins of 3 to about 20 carbon atoms (e.g. propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene and/or styrene), preferably alpha-olefins of 3 to about 10 carbon atoms, and more preferably these polymers are a copolymer of ethylene and 1-octene.

The density of these substantially linear ethylene polymers is typically between about 0.850 to about 0.935 grams per cubic centimeter ( $\text{g/cm}^3$ ), preferably about 0.860 to about 0.900  $\text{g/cm}^3$ . Their melt flow ratio, measured as  $I_{10}/I_2$ , is greater than or equal to 5.63, is preferably from about 6.5 to 15, and is more preferably from about 7 to 10.  $I_2$  is measured according to ASTM Designation D 1238, Condition 190/2.16, and  $I_{10}$  according to Condition 190/10.0. Their molecular weight distribution [weight average molecular weight divided by number average molecular weight ( $M_w/M_n$ )], measured by gel permeation

chromatography (GPC), is defined by the equation:  $M_w/M_n \leq (I_{10}/I_2) - 4.63$ , and is preferably between about 1.5 and 2.5. For substantially linear ethylene polymers, the  $I_{10}/I_2$  ratio indicates the degree of long-chain branching, i.e. the larger the  $I_{10}/I_2$  ratio, the more long-chain branching in the polymer.

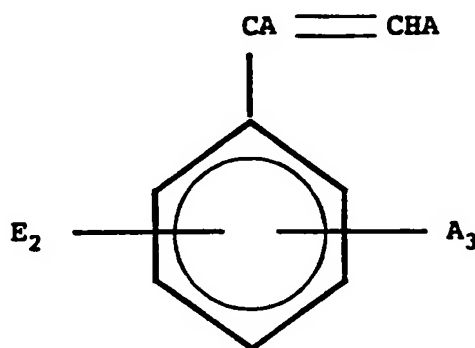
According to Ramamurthy in 30(2) *Journal of Rheology* 337-357 (1986), polymer surface melt fracture may occur above a certain critical flow rate, which may result in irregularities ranging from loss of specular gloss to the more severe form of "sharkskin". As used herein, the onset of surface melt fracture is characterized as the beginning of loss of extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The substantially linear ethylene polymers hereof are further characterized by a critical shear rate at the onset of surface melt fracture which is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same  $I_2$  and  $M_w/M_n$ .

The unique characteristic of these homogeneously branched, substantially linear ethylene polymers is a highly unexpected flow property wherein the  $I_{10}/I_2$  value of the polymer is essentially independent of the polydispersity index (i.e.  $M_w/M_n$ ) of the polymer. This is contrasted with conventional linear homogeneously branched and linear heterogeneously branched polyethylene resins having rheological properties such that to increase the  $I_{10}/I_2$  value, the polydispersity index must also be increased.

The preferred  $I_2$  melt index for these substantially linear ethylene polymers is from about 0.01 g/10 min to about 100 g/10 min, and more preferably about 0.1 to 10 g/10 min. Typically, these polymers are homogeneously branched and do not have any measurable high density fraction, i.e. short chain branching distribution as measured by Temperature Rising Elution Fractionation which is described in USP 5,089,321 (incorporated herein in its entirety). Stated in another manner, these polymers do not contain any polymer fraction that has a degree of branching less than or equal to 2 methyls/1000 carbons. These substantially linear ethylene polymers are also characterized by a single differential scanning calorimetry (DSC) melting peak.

Component (c) in the compositions of this invention is a styrenic copolymer prepared from one or more styrenic monomers and one or more ethylenically unsaturated monomers copolymerizable with a styrenic monomer. The styrenic copolymer may be a random, alternate, block or grafted copolymer, and a mixture of more than one styrenic copolymer may be used as well.

Styrenic monomers of particular interest for use in preparation of a styrenic copolymer, in addition to styrene itself, include one or more of the substituted styrenes or vinyl aromatic compounds described by the following formula [it being understood that a reference to "styrene" as a comonomer in component (c) is to be read as a reference to any of the styrenic or vinyl aromatic monomers described herein or any others of like kind]:



wherein each A is independently hydrogen, a C<sub>1</sub>-C<sub>6</sub> alkyl radical or a halogen atom such as chlorine or bromine; and each E is independently hydrogen, a C<sub>1</sub>-C<sub>10</sub> alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy radical, a halogen atom such as chlorine or bromine, or two E's may be joined to form a naphthalene structure. Representative examples of suitable styrenic monomers, in addition to styrene itself, include one or more of the following: ring-substituted alkyl styrenes; ring-substituted halostyrenes; ring-alkyl, ring-halo-substituted styrenes; and vinyl naphthalene or anthracene.

Ethylenically unsaturated monomers of particular interest for copolymerization with a styrenic monomer include one or more of those described by the formula:  $D-CH=C(D)-(CH_2)_n-G$ , wherein each D independently represents a substituent selected from the group consisting of hydrogen, halogen (such as fluorine, chlorine or bromine),  $C_1-C_6$  alkyl or alkoxy, or taken together represent an anhydride linkage; G is hydrogen, vinyl,  $C_1-C_{12}$  alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, arylalkyl, alkoxy, aryloxy, kotoxy, halogen (such as fluorine, chlorine or bromine), cyano or pyridyl; and n is 0-9.

10

Representative examples of ethylenically unsaturated monomers copolymerizable with a styrenic monomer are those which bear a polar or electronegative group and include one or more of the following: a vinyl nitrile compound; a diene; a  $C_2-C_{10}$  alkylene compound including halo-substituted derivatives thereof; the alpha,beta-ethylenically unsaturated carboxylic acids and their anhydrides and  $C_1 - C_{10}$  alkyl, aminoalkyl and hydroxyalkyl esters and amides; an aliphatic or aromatic maleimide; vinyl ketones; vinyl or allyl acetate and higher alkyl or aryl vinyl or allyl esters; vinyl alcohols; vinyl ethers and their alkyl-substituted or halo derivatives; and an oxazoline compound.

20

Examples of preferred styrenic copolymers are vinyl aromatic/vinyl nitrile copolymers such as styrene/acrylonitrile copolymer ("SAN"), styrene/maleic anhydride copolymer, styrene/glycidyl methacrylate copolymer, aryl maleimide/vinyl nitrile/diene/styrenic copolymer, styrene/alkyl methacrylate copolymer, styrene/alkyl methacrylate/glycidyl methacrylate copolymer, styrene/butyl acrylate copolymer, methyl methacrylate/acrylonitrile/butadiene/styrene copolymer, or a rubber-modified vinyl aromatic/vinyl nitrile copolymer such as an ABS, AES or ASA copolymer.

30

ABS (acrylonitrile/butadiene/styrene copolymer) is an elastomeric-thermoplastic composite in which vinyl aromatic/vinyl nitrile copolymer is grafted onto a polybutadiene substrate latex. The polybutadiene forms particles of rubber - the rubber modifier or elastomeric component - which are dispersed as a discrete phase in a thermoplastic matrix formed by random vinyl aromatic/vinyl nitrile copolymer. Typically, vinyl aromatic/vinyl nitrile copolymer is both

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occluded in and grafted to the particles of rubber. AES  
(acrylonitrile/EPDM/styrene) copolymer is a styrenic copolymer which is  
obtained when vinyl aromatic/vinyl nitrile copolymer is rubber-modified  
by grafting vinyl aromatic/vinyl nitrile copolymer to a substrate made  
5 up of an EPDM (ethylene/propylene/non-conjugated diene) rubber. A vinyl  
aromatic/vinyl nitrile copolymer can also be crosslinked to an alkyl  
acrylate elastomer to form a rubber-modified styrenic copolymer, as in  
the case of an ASA (acrylonitrile/styrene/acrylate) copolymer.

10 A styrenic copolymer may be made by an emulsion, suspension or  
mass (bulk) method.

Component (d) in the compositions of this invention is a  
supplemental impact modifier, including, for example, elastomers such as  
15 a block copolymer, a core-shell grafted copolymer or mixtures thereof.

A block copolymer useful as a supplemental impact modifier  
herein can be either linear, branched, radial or teleblock, and can be  
either a di-block ("A-B") copolymer, tri-block ("A-B-A") copolymer, or  
20 radial teleblock copolymer with or without tapered sections, i.e. portions  
of the polymer where the monomers alternate or are in random order close  
to the point of transition between the A and B blocks.

The A portion is frequently prepared by polymerizing one or  
25 more vinyl aromatic hydrocarbon monomers such as the various styrenic  
monomers described above with respect to a styrenic copolymer; has a  
weight average molecular weight of about 4,000 to about 115,000; and has  
properties characteristic of thermoplastic substances in that it has the  
stability necessary for processing at elevated temperatures and yet  
30 possesses good strength below the temperature at which it softens. The  
B portion of the block copolymer typically results from polymerizing  
substituted or unsubstituted  $C_3$ - $C_{10}$  dienes, particularly conjugated  
dienes such as butadiene or isoprene; has a weight average molecular  
weight of about 20,000 to about 450,000; and is characterized by  
35 elastomeric properties which allow it to absorb and dissipate an  
applied stress and then regain its shape.

To reduce oxidative and thermal instability, the block copolymers used herein can also desirably be hydrogenated to reduce the degree of unsaturation on the polymer chain and on the pendant aromatic rings.

5

The most preferred vinyl aromatic block copolymers are vinyl aromatic/conjugated diene block copolymers formed from styrene and butadiene or styrene and isoprene. When the styrene/butadiene copolymers are hydrogenated, they are frequently represented as styrene/((ethylene/butylene) copolymer in the di-block form, or as  
10 styrene/((ethylene/butylene)/styrene copolymer in the tri-block form. When the styrene/isoprene copolymers are hydrogenated, they are frequently represented as styrene/((ethylene/propylene) copolymer in the di-block form, or as styrene/((ethylene/propylene)/styrene copolymer in  
15 the tri-block form. Vinyl aromatic/diene block copolymers such as are described above are available commercially as the various Kraton™ elastomers from Shell Chemical Company.

Core-shell grafted copolymer elastomers suitable for use  
20 herein as a supplemental impact modifier are those which are based on either a diene rubber, an alkyl acrylate rubber, or on mixtures thereof, and have an elastomeric, or rubber, phase which is greater than about 45% or more of the copolymer by weight. A core-shell grafted copolymer based on a diene rubber contains a substrate latex, or core, which is  
25 made by polymerizing a diene, preferably a conjugated diene, or by copolymerizing a diene with a mono-olefin or a polar vinyl compound, such as styrene, acrylonitrile, or an alkyl ester of an unsaturated carboxylic acid such as methyl methacrylate. A mixture of ethylenically unsaturated monomers is then graft polymerized to the substrate latex.  
30 A variety of monomers may be used for this grafting purpose, of which the following are exemplary: vinyl aromatics; vinyl nitriles; a C<sub>1</sub>-C<sub>8</sub> alkyl acrylate or methacrylate; glycidyl methacrylate; acrylic or methacrylic acid; and the like or a mixture of two or more thereof. The preferred grafting monomers include one or more of styrene,  
35 acrylonitrile and methyl methacrylate.

A core-shell grafted copolymer based on an alkyl acrylate rubber has a first phase forming an elastomeric core and a second phase

forming a rigid thermoplastic phase about said elastomeric core. The elastomeric core is formed by emulsion or suspension polymerization of monomers which consist of at least about 50 weight percent alkyl and/or aralkyl acrylates having up to fifteen carbon atoms, and, although  
5 longer chains may be used, the alkyls are preferably  $C_2-C_6$ , most preferably butyl acrylate. The rigid thermoplastic phase of the acrylate rubber is formed on the surface of the elastomeric core using suspension or emulsion polymerization techniques. The monomers necessary to create this phase include ethylenically unsaturated  
10 monomers such as glycidyl methacrylate, or an alkyl ester of an unsaturated carboxylic acid, for example a  $C_1-C_8$  alkyl acrylate or methacrylate such as methyl methacrylate, or mixtures of any of the foregoing.

15 Other supplemental impact modifiers or elastomers useful in the compositions of this invention are those based generally on a long-chain, hydrocarbon backbone ("olefinic elastomers"), which may be prepared predominantly from various mono- or dialkenyl monomers and may be grafted with one or more styrenic monomers. Representative examples  
20 of a few olefinic elastomers which illustrate the variation in the known substances which would suffice for such purpose are as follows: butyl rubber; chlorinated polyethylene rubber; chlorosulfonated polyethylene rubber; an olefin polymer or copolymer such as ethylene/propylene copolymer, ethylene/styrene copolymer or ethylene/propylene/diene  
25 copolymer, which may be grafted with one or more styrenic monomers; neoprene rubber; nitrile rubber; polybutadiene and polyisoprene.

An example of a preferred olefinic elastomer is a copolymer prepared from (i) at least one olefin monomer such as ethylene,  
30 propylene, isopropylene, butylene or isobutylene, or at least one conjugated diene such as butadiene, and the like, or mixtures thereof; and (ii) an ethylenically unsaturated monomer carrying an epoxide group (for example, glycidyl methacrylate), and, optionally, (iii) an ethylenically unsaturated monomer which does not carry an epoxide group  
35 (for example, vinyl acetate).



Component (e) in the compositions of this invention is a molding polymer selected from (i) polyester, (ii) other olefin-based polymers, and mixtures thereof.

5           Component (e)(i), a polyester, as utilized in the compositions of this invention may be made, for example, by the self-esterification of hydroxycarboxylic acids, or by direct esterification, which involves the step-growth reaction of a diol with a dicarboxylic acid with the resulting elimination of water, giving a polyester with an  $[-AABB-]$ -  
10 repeating unit.

Suitable reactants for making the polyester used in this invention, in addition to hydroxycarboxylic acids, are diols and dicarboxylic acids either or both of which can be aliphatic or aromatic.  
15 A polyester which is a poly(alkylene alkanedicarboxylate), a poly(alkylene arylenedicarboxylate), a poly(arylene alkanedicarboxylate), or a poly(arylene arylenedicarboxylate) is therefore appropriate for use herein. Alkyl portions of the polymer chain can be substituted with, for example, halogens,  $C_1-C_8$  alkoxy groups or  $C_1-C_8$  alkyl side chains, and can contain divalent heteroatomic  
20 groups (such as  $-O-$ ,  $-Si-$ ,  $-S-$  or  $-SO_2-$ ) in the paraffinic segment of the chain. The chain can also contain unsaturation and  $C_6-C_{10}$  non-aromatic rings. Aromatic rings can contain substituents such as halogens,  $C_1-C_8$  alkoxy or  $C_1-C_8$  alkyl groups, and can be joined to the  
25 polymer backbone in any ring position and directly to the alcohol or acid functionality or to intervening atoms.

Typical aliphatic diols used in ester formation are the  $C_2-C_{10}$  primary and secondary glycols. Alkanedicarboxylic acids frequently used  
30 are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be, for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexane-dimethylene glycol, resorcinol, or one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl)propane. Aromatic diacids include, for example, terephthalic acid, isophthalic acid,  
35 naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, and diphenylsulfonedicarboxylic acid.

In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable for use in this invention, and are all included in the term "polyester".

Aromatic polyesters, those prepared from an aromatic diacid, such as the poly(alkylene arylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention.

Component (d)(ii) includes a variety of olefin-based polymers which are not part of the category of substantially linear ethylene polymers described above as component (b). These other olefin-based polymers include conventional homogeneously or heterogeneously branched linear ethylene polymers, any of which can be grafted or ungrafted. Examples of such polymers include high density polyethylene, low density polyethylene, linear low density polyethylene, ultra low density polyethylene, polypropylene, polyisobutylene, ethylene/acrylic acid copolymer, ethylene/vinyl acetate copolymer, ethylene/vinyl alcohol copolymer, ethylene/carbon monoxide copolymer (including those described in USP 4,916,208 and 4,929,673), ethylene/propylene/carbon monoxide copolymer, ethylene/carbon monoxide/acrylic acid copolymer, polystyrene, poly(vinyl chloride), and the like and mixtures thereof.

A variety of additives may be advantageously employed to promote flame retardance or ignition resistance in the compositions of this invention, or as antimicrobial agents; antioxidants; antistatic agents; fillers and reinforcing agents; hydrolytic stabilizers; lubricants; mold release agents; pigments, dyes and colorants; plasticizers; heat stabilizers; ultraviolet light stabilizers. A preferred hindered phenolic antioxidant is Irganox™ 1076 antioxidant, available from Ciba-Geigy Corp. Such additives, if used, typically do not exceed 45 percent by weight of the total composition, and are advantageously from about 0.001 to 15 percent, preferably from about

0.01 to 10 percent and more preferably from about 0.1 to 10 percent, by weight of the total composition.

To illustrate the practice of this invention, examples of several preferred embodiments are set forth below, however, these examples (Examples 1-3) do not in any manner restrict the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of Examples 1-3 with those of various controlled formulations (Controls A-H) which do not possess the features of, and are not therefore embodiments of, this invention.

The compositions of Examples 1-3 and Controls A-H are prepared by mixing the dry components on paint shaker for 5 minutes, and then feeding the dry-blended formulation to a 30 mm Werner & Pfleiderer extruder set at 280°C barrel zone temperature, 250 rpm and 70-85% torque. The extrudate is cooled in the form of strands and is then comminuted as pellets. The pellets are dried in an air draft oven for 3 hours at 120°C, and are then used to prepare test specimens on a 70 ton Arburg molding machine having temperature zone settings of 150°C, 200°C, 250°C, 250°C and 250°C, and a mold temperature of 80°C.

The formulation content of Example 1 and Controls A-E is given below in Table I, in parts by weight of the total composition. In Table I:

"Polycarbonate" is a Bisphenol-A polycarbonate having a weight average molecular weight of 28,000;

"LLDPE I" is a linear low density polyethylene having a melt index, according to ASTM D 1238, of 2;

"LLDPE II" is a linear low density polyethylene having a melt index, according to ASTM D 1238, of 26;

"EPR" is a copolymer of 45 weight percent ethylene and 55 weight percent propylene;

"MBS" is methacrylate/styrene/butadiene copolymer (Paraloid™ 8963 from Rohm & Haas); and

"ITP" is a substantially linear ethylene polymer, as described above as component (b), having a density of approximately 0.87 g/cm<sup>3</sup>.

The following tests are performed on Example 1 and Controls A-E, and the results of these test are also shown in Table I:

Impact resistance is measured by the Izod test ("Izod") according to ASTM Designation D 256-84 (Method A) at -35°C. The notch is 10 mils (0.254 mm) in radius. Impact is perpendicular to the flow lines in the plaque from which the bar is cut. Izod results are reported in ft-lb/in.

Impact resistance is also measured by the Izod test ("Weldline") according to ASTM Designation D 256-84 (Method A) at room temperature (23-25°C), but with respect to a sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Weldline results are also reported in ft-lb/in.

Percent elongation at break is measured in accordance with ASTM Designation D 638-84 at a rate of 2"/minute with respect to a tensile bar which has been placed under 0.5 percent strain while submerged in a bath of 60 weight percent isooctane and 40 weight percent toluene for 5 minutes. After removal from the bath the sample is allowed to dry without strain for at least 24 hours before testing.

Percent elongation at break is also measured with respect to a tensile bar which has not been subjected to the solvent bath. Results are expressed as "Elongation/soak" and "Elongation/dry", respectively.

Percent of length retention ("Retention") is calculated by dividing the percent elongation value obtained as to a sample which has received the solvent bath, as described above (Elongation/soak), by the percent elongation value obtained as to sample of the same formulation which has not received the solvent bath (Elongation/dry).

"Viscosity" is determined by placing a disc molded from the composition between two plates, each of which rotates reciprocatingly through an arc of 0.1 radian with a frequency of one second while the disc is held at 270°C. The power consumption required to maintain the stated arc and frequency is proportional to the viscosity of the composition. Viscosity is stated in poise.

**Table I, Content and Properties  
of Controls A-E and Example 1**

	Controls					Example 1
	A	B	C	D	E	
Polycarbonate	100	95	95	95	95	95
LLDPE I		5				
LLDPE II			5			
EPR				5		
MBS					5	
ITP						5
-35°C Izod (ft-lb/in)	2.8	1.9	2.3	3.7	12.3	10.6
RT Weldline (ft-lb/in)	45	5	8		38	26
Elongation/soak (%)	8	88	98	159	11	120
Elongation/dry (%)	210	96	105	169	44	112
Retention (%)	4	92	93	94	25	107
Viscosity (poise)					10,000	8,500

The data in Table I demonstrate that while polycarbonate has high impact strength in certain aspects, it has very little solvent resistance. Addition of an olefin-based modifier to polycarbonate, such as LLDPE or EPR, definitely results in a composition having solvent resistance which is much improved over that of polycarbonate, but what little impact strength polycarbonate possesses by itself is almost completely sacrificed, as indicated by the weldline values. Use of MBS as a modifier in a composition with polycarbonate produces a material which has unassailable impact strength, but which has poor solvent resistance. By contrast, Example 1, in which polycarbonate is blended with a substantially linear ethylene polymer, shows a desirable balance of relatively good values in both the properties of impact resistance and solvent resistance, and overcomes the problem caused by previous modifiers which, while improving one property of polycarbonate, caused an offsetting decline in other properties. Example 1 shows no tendency

toward delamination, and the lower viscosity of Example 1 makes it easier to process.

The formulation content of Examples 2-3 and Controls F-H is given below in Table II, in parts by weight of the total composition. In Table II:

"Polycarbonate" is a Bisphenol-A polycarbonate having a weight average molecular weight of 23,000;

"MBS" is methacrylate/styrene/butadiene copolymer (Paraloid<sup>™</sup> 8963 from Rohm & Haas);

"HDPE" is high density polyethylene;

"GRC" is a grafted core-shell elastomer prepared from acrylonitrile, butadiene and styrene; and

"ITP" is a substantially linear ethylene polymer, as described above as component (b), having a density of approximately 0.87 g/cm<sup>3</sup>.

The following tests are performed on Example 2-3 and Controls F-H, and the results of these test are also shown in Table II:

The Izod and Weldline tests are performed as described above.

"PP" indicates that the impact is perpendicular to the flow lines in the plaque from which the bar is cut. "PL" indicates that the impact is parallel to the flow lines in the plaque from which the bar is cut.

Deflection temperature under load ("D.T.U.L.") is measured in accordance with ASTM Designation D 648-82 at 66 psi.

Tensile strength at yield ("Yield"), tensile strength at break ("Break"), and percent elongation at break ("Elongation"), and tensile modulus ("T. Modulus") are all determined according to ASTM Designation D 638. All except elongation are reported in psi.

Flexural modulus ("F. Modulus") is determined according to ASTM D 790. Results are reported in psi.

**Table II, Content and Properties  
of Controls F-H and Examples 2-3**

	Control F	Example 2	Control G	Control H	Example 3
Polycarbonate	95	95	92	92.5	92.5
MBS	2.5	2.5			
HDPE	2.5			2.5	
GRC			8	5	5
ITP		2.5			2.5
Izod, 23°C, PP (ft-lb/in)	11.8	11.7	12.7	11.7	11.9
Izod, -30°C, PL (ft-lb/in)	4.3	11.8	4.3	4.1	6.5
Izod, -30°C, PP (ft-lb/in)	4.4	11.8	4.1	4.0	8.7
Weldline, RT (ft-lb/in)	30.1	23.8	12.4	20.4	20.8
D.T.U.L. (°C)	123.5	123.3	123.3	122.3	121.8
Yield (psi)	8040	8110	8260	7880	7760
Break (psi)	7096	7167	7405	7408	8002
Elongation (%)	100	100	110	112	128
T. Modulus (psi)	248,000	250,000	259,000	236,000	231,000
F. Modulus (psi)	329,000	327,000	340,000	324,000	330,000

A review of the data in Table II concerning Controls F-H and Examples 2-3 indicates that blending even a small amount of a substantially liner ethylene polymer in a polycarbonate composition containing a conventional impact modifier yields a composition having a desirable balance of several properties. For instance, when HDPE in Control F is replaced with a substantially liner ethylene polymer, the resulting composition, Example 2, shows distinctly improved low temperature Izod. While there is a decrease in Weldline as to Example 2, the value remains at an acceptable level, and other properties show essentially comparable values. Similarly, when a portion of the GRC in Control G, or all of the HDPE in Control H, is replaced with a substantially liner ethylene polymer, the resulting composition, Example 3, shows improved low temperature Izod, tensile strength at break and

Elongation while maintaining an acceptable level of performance as to the other properties. In addition, Examples 2-3 show no tendency toward delamination.

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1. A composition of matter comprising, in admixture, (a) polycarbonate, and (b) a substantially linear ethylene polymer which has:

(i) a melt flow ratio,  $I_{10}/I_2$ , which is greater than or equal to 5.63;

(ii) a molecular weight distribution,  $M_w/M_n$ , which is less than or equal to the value:  $(I_{10}/I_2) - 4.63$ ; and

(iii) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same  $I_2$  and same  $M_w/M_n$ .

2. The composition of Claim 1 further comprising a styrenic copolymer.

3. The composition of Claim 2 wherein the styrenic copolymer is a rubber-modified vinyl aromatic/vinyl nitrile copolymer.

4. The composition of Claim 3 wherein the rubber-modifier in the rubber-modified vinyl aromatic/vinyl nitrile copolymer is polymerized from a diene, an olefin monomer, an alkyl acrylate or methacrylate, or a mixture thereof, or a mixture of one or more of the foregoing with a vinyl aromatic compound or a vinyl nitrile compound.

5. The composition of Claim 3 wherein the rubber-modified vinyl aromatic/vinyl nitrile copolymer is acrylonitrile/butadiene/styrene copolymer.

6. The composition of Claim 1 further comprising an elastomeric impact modifier selected from a vinyl aromatic/diene block copolymer, a core-shell grafted copolymer, or a mixture thereof.

7. The composition of Claim 1 further comprising a polyester.

8. The composition of Claim 7 further comprising a styrenic copolymer.

9. The composition of Claim 7 further comprising an elastomeric impact modifier selected from a vinyl aromatic/diene block copolymer, a core-shell grafted copolymer, or a mixture thereof.

10. The composition of Claim 1 further comprising an olefin molding polymer.

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11. The composition of Claim 1 wherein the substantially linear ethylene polymer has a density greater than about  $0.850 \text{ g/cm}^3$ .

12. The composition of Claim 1 wherein the substantially linear ethylene polymer has a melt flow ratio,  $I_{10}/I_2$ , of about 6.5 to 15.

13. The composition of Claim 1 wherein the substantially linear ethylene polymer has a molecular weight distribution ( $M_w/M_n$ ) of about 1.5 to 2.5.

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14. The composition of Claim 1 further comprising a filler.

15. The composition of Claim 1 in the form of a molded or extruded article.

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# INTERNATIONAL SEARCH REPORT

Inter. Appl. No. PCT/US 95/06194

## A. CLASSIFICATION OF SUBJECT MATTER

C 08 L 69/00, (C 08 L 69/00, C 08 L 23:06, C 08 L 25:12,  
C 08 L 51:04, C 08 L 55:02)

According to International Patent Classification (IPC) or to both national classification and IPC 6

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 L, C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5 278 272 (LAI et al.) 11 January 1994 (11.01.94), column 1 - column 2, line 62; column 3, lines 1-23; column 15, lines 47-56; claims. --	1-3, 8, 10, 11-15
A	US, A, 5 308 894 (LAUGHNER) 03 May 1994 (03.05.94), column 2, line 53 - column 3, line 68; claims. --	1-10, 14, 15
A	US, A, 5 194 495 (LUNDY et al.) 16 March 1993 (16.03.93), column 1 - column 2, line 19; examples; claims.	1-10, 14, 15

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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- \* "A" document defining the general state of the art which is not considered to be of particular relevance
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- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

\* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* "A" document member of the same patent family

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04 August 1995

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# INTERNATIONAL SEARCH REPORT

-2-

International Application No

PCT/US 95/06194

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p style="text-align: center;">--</p> <p>US, A, 5 089 321            (CHUM et al.) 18 February            1992 (18.02.92),            column 2, lines 3-24;            examples; claims            (cited in the application).  <p style="text-align: center;">----</p></p>	<p>1,            10-15</p>

# ANHANG

zum Internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

# ANNEX

to the International Search  
Report to the International Patent  
Application No.

# ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 95/06194 SAE 110285

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentedokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
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relatifs aux documents de brevets cités  
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